

ULTRA LOW CONCENTRATION ADSORPTION EQUILIBRIA

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ABSTRACT

This paper discusses innovative research on the subject of protecting the warfighter from hazardous vapors by means of employing chemical filters containing microporous, nano-structured sorbents. Specifically this work focuses on novel experimental and modeling methods to characterize and predict at ultra-low chemical vapor concentrations the protection afforded by adsorption-based vapor filtration systems. The motivation for this work is to provide appropriate respiratory protection for the warfighter at pace with a changing health regulatory environment where exposure limit values have decreased, particularly for the workplace and general population. Recently, air pollution abatement and toxic industrial chemical exposure concerns have broadened the interest in vapor filtration, especially in the determination of estimates used in the prediction of breakthrough times and filter element replacement. This work directly addresses these issues and should lead to a substantial increase in confidence about estimates of low-level breakthrough times for standard adsorption-based vapor filter systems and a better understanding of the adsorption process at ultra-low concentrations. Similar data have been used in the design and construction of GB and HD Solid-State Vapor Generators for U.S. Army Chemical Materials Agency as calibration devices for their workplace air monitors.

Results are presented for procedures to prepare adsorbent samples for accurate ultra-low concentration adsorption equilibrium measurements. We have uniformly loaded and measured AE data for the following adsorbate-adsorbent pairs: GB on Amborsorb 572 at 2, 2.5 and 4.5 wt% loading and HD on Amborsorb 563 at 10, 14 and 17% loading at three temperatures and n-pentane, n-hexane, n-octane and n-decane on BPL activated carbon between 0.01 to 10.0% loadings at temperatures from 0 to 100C. The transition from pore filling behavior to the low-concentration, linear, Henry's Law (HL) behavior for moderate volatility CW agent vapors of GB, HD and a homologous series of unbranched hydrocarbons are discussed. A modified Dubinin-Radushkevich (DR) approach is used to account for the HL low-concentration limit. This particular form of the theory is used to predict the HL adsorption behavior of a toxic vapor and

potentially to predict the HL behavior of a toxic vapor from the adsorption equilibrium of a similar toxic vapor.

1. INTRODUCTION

Several years ago, interest in measuring low-end AE data was stimulated by work performed for the US Army Chemical Materials Agency. The issue was the performance of a proposed incinerator effluent filtration system, particularly for removal of low-volatility compounds of environmental concern, e.g., polychlorinated dioxins and furans. Since the allowable emission level for those materials was equivalent to relative pressures several orders of magnitude below what was possible at that time, methods to measure AE data in this range were investigated. Standard methods for measurement of such data included volumetric, in which a known amount of adsorbate is injected into a closed system with a known amount of adsorbent and the loading is inferred based on residual vapor phase concentration after equilibration, and gravimetric, in which the adsorbent is exposed to a fixed concentration of vapor and the mass increase is measured. During the course of the latter experimentation, it was observed that the rate of desorption between data measurement points was slow, and that the desired AE data could be inferred from the measured concentration during a purge step. Further, it was recognized that the detection limit for that approach was only limited by existing analytical methods, which could be below the part-per-trillion (ppT) concentration range in favorable cases.

For low- and intermediate-volatility materials, such as G-type nerve agents, the analytical methodology is highly evolved and sub-ppT concentration measurements are possible. This recognition led directly to experiments using simulants and GB (isopropyl methylphosphonofluoridate, in which AE data in the 10^{-10} relative pressure range were reported, representing an improvement of nearly four orders of magnitude below any previously reported in the literature. Since it is known that the standard (DR) AE correlations have inappropriate low-concentration limits, it was of interest to determine whether the transition from DR to HL was observable in this range. Since it was not, accurate performance modeling at low concentration limits is still constrained by this uncertainty, and the current effort was initiated in order to further extend the low-concentration limits of AE data to directly observe this expected transition and lay the groundwork for understanding these phenomena. The development of sample preparation and processing techniques in this study provides a strong foundation for interpretation of low-concentration adsorption behavior.

The ultra-low-level equilibrium data have already been used in the design and construction of GB and HD Solid-State Vapor Generators for U.S. Army

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Chemical Materials Agency as calibration devices for their workplace air monitors and as a training device by the U.S. Customs and Border Control Agency under an interagency agreement to facilitate training relative to their Chemical Detector Dog program. In addition, a new technology has been developed at Vanderbilt University to load and equilibrate adsorbent and trace adsorbates in sealed ampules. This process offers a convenient route for the batch preparation and long-term storage of chemical loaded adsorbents used for adsorption research.

The Dubinin-Radushkevich (DR) equation, a particular form of the Polanyi Potential theory, has been demonstrated for GB at relative pressures (partial pressure divided by the vapor pressure), in the 10^{-10} range, corresponding to a partial pressures in the 10^{-7} Pa range, Karwacki et. al., 1999. In that work, the range of AE data was extended by four orders of magnitude to a lower vapor phase concentration than previously reported. However, the expected deviation from the DR correlation was not observed. While that is an encouraging result from an operational point of view, it should be recognized that concerns relative to lower exposure concentrations, i.e., sub-ppT in some cases, are growing. As a result, exposure limit values have decreased, particularly for the workplace and general population. The principal means to mitigate toxic chemical exposure risk is through the use of adsorption-based vapor filtration systems. Recently, air pollution abatement and toxic industrial chemical exposure concerns have broadened the interest in vapor filtration, especially in the determination of estimates used in the prediction of breakthrough times and filter element replacement. This work directly addresses these issues, leading to a substantial increase in confidence about estimates of low-level breakthrough times for standard adsorption-based vapor filter systems and a better understanding of the adsorption process at ppT concentrations and below.

In the limit of low loading an isotherm should have a finite, linear slope (Henry's law). This is true even for a heterogeneous surface, such as activated carbon. What is needed in the low region for Henry's law is only for molecules to be acting independently of one another as they adsorb and desorb, thus exploring the surface. It must be determined if there is a modification that can be applied to standard correlations to incorporate the Henry's Law limit as well as explore the relationship between physical parameters (e.g., volatility and solubility) and the transition point.

For nanoporous adsorbents, e.g., BPL carbon, which exhibit pore filling as the result of the superposition of potentials of opposing walls, an isotherm can be interpreted in terms of a pore size distribution and vice versa. ("Pore size distribution" and "energy distribution" can be used interchangeably. The DR is

based on a particular energy distribution.) This means that the measured isotherm on these adsorbents reflects the pore size distribution. If only the top part of an isotherm is known, then only that part of the pore size distribution filled in that range can be determined from the data. The smaller pores will be filled at the bottom or lower concentration end of the isotherm.

Isotherm equations will predict equilibrium all the way down to zero loading corresponding to pore size distributions with pores impossibly small for a molecule to enter. There is no reason to believe that this pore size distribution is accurate in the low range if it has not been confirmed by data. This means that one cannot predict where data will begin to deviate from an isotherm equation. It must be measured. Deviations from the DR equation for a molecule (like n-pentane) on a particular adsorbent are significant, because it can be expected that other molecules (like n-pentane, n-hexane, n-octane, n-decane, or CWA) will deviate from the DR equation to that same extent of pore filling, because that indicates the true pore size distribution which is likely different from the underlying pore size distribution in the DR equation.

Adsorbents have different pore size distributions, where a measured isotherm breaks from the DR equation (like n-pentane on BPL carbon) will not necessarily be where the break occurs for a different adsorbent (like n-pentane on a particular Ambersorb, a synthetic carbon). The break may be at close to the same point, where the number density of molecules is similar and the isotherm is becoming more linear. Some estimates of where the theories are approaching Henry's law behavior can be seen in the figures. The theories that do have the proper Henry's limit predict close to linear behavior in a region experimentally accessible. Thus, possible breaks from the DR equation are suggested. There have been a number of papers trying to deal with the Henry's Law shortcomings of the DR equation. Mahle, 1997, identified the point where the theory started to deviate as the point where the slope of the curve, dn/dP , is equal to the loading over the pressure, n/P . A tangent line is then drawn from this point through the origin. Kapoor et al., 1989, introduced a linear term and two weighting factors. The two weighting factors are inversely proportional, such that the linear term is dominant in the Henry's Law region and is of minor consequence at higher pressure. Chen and Yang, 1994, re-derived the equations using statistical thermodynamics.

The adsorption group contribution theory (GCT), Walton et al. 2004 and Ding and LeVan, uses a two-dimensional patch-wise heterogeneous hexagonal lattice to represent the adsorption surface. The adsorbate is broken down into three elemental groups for unbranched hydrocarbons: CH_2 , CH_3 , and CH_4 . As an example, hexane would contain 2 CH_3 groups and 4 CH_2 groups.

There are 11 different parameters that can be fit for the model. These parameters fall into two different categories, eight parameters describe the adsorbate molecules and three parameters describe the adsorbent. The parameters were fit using adsorption data for methane, ethane, butane, and n-hexane at multiple temperatures. It has been demonstrated that the theory can be extended to other molecules; predictions for propane and n-octane were shown to be accurate. The theory also works at multiple temperatures, and for mixtures of hydrocarbons. This theory has a correct Henry's Law limit.

Virtual group theory (VGT), Ding 2002, treats adsorption as a mixture of the adsorbate and a virtual group, in this case carbon representing the adsorbent. The mixture is then treated using the UNIFAC theory, equation of state, which allows the adsorbate to be built by its component parts. Using the vapor pressure the virtual mole fraction is calculated using solution thermodynamics, and then a mole fraction for a probe component is calculated. From the mole fraction of the probe component, a vapor pressure for the probe component is calculated. Using the vapor pressure of the probe component, a reference loading for the probe component is calculated using an isotherm equation, and a filling fraction is calculated from this reference loading. The loading of the adsorbate is then calculated from the filling fraction.

The use of the UNIFAC equation of state allows this method to be a very powerful method for predicting adsorption behavior. Once the adsorption behavior for various different functional groups is known, the adsorption behavior for molecules containing those functional groups can be calculated. The density of the virtual group is a function of the pore geometry, surface heterogeneity and the filling fraction. This theory has a correct Henry's Law limit.

A critical feature of this work is to use data collected from this effort to develop a predictive tool for a wide variety of adsorbates. A modification of the DR correlation to make it compatible with a low-concentration limit exists; however, the point of divergence and understanding have not resulted owing to the prior lack of data such as those sought in this work. Measure adsorption equilibrium of agents and simulants at extremely low vapor-phase concentrations ($<<10^{-6}$, relative pressure, P_i/P_{sat} , partial pressure divided by the vapor pressure) and loadings (<0.01 wt %), while minimizing or eliminating the effects of hydrolysis and thermal decomposition. The transition will be observed from pore filling behavior to the low-concentration, linear, Henry's Law (HL) behavior for moderate volatility CW agent vapors of GB, HD and a homologous series of unbranched hydrocarbons. Using a modified Dubinin-

Radushkevich (DR) approach to account for the HL low-concentration limit, develop the underlying theory to predict the HL adsorption behavior of a toxic vapor and potentially to predict the HL behavior of a toxic vapor from the adsorption equilibrium of a similar toxic vapor.

2. EXPERIMENTAL

The apparatus to prepare adsorbent samples for ultra-low concentration adsorption equilibrium measurements is shown in Figure 1. Ampoules filled with adsorbent are evacuated. A dose of liquid is flashed to the head-space of the ampule where it adsorbs. The rotation of the sample holder promotes equal distribution of the vapor on the adsorbent. Equilibrated samples are removed from ampoules in a glove box and loaded into tubes for desorption. A metered flow at a controlled temperature is used to desorb a small fraction of the adsorbate. Vapor phase concentrations are measured using gas chromatograph with pre-concentrator. Care must be taken to confirm that the desorption step is not rate limited, but is rather at equilibrium. The desorption is determined at several velocities to confirm absence of rate effects.

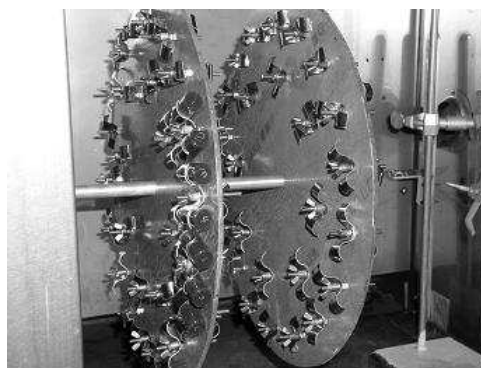


Figure 1. Conditioning apparatus with sample vials attached.

Equilibrated samples are removed from ampoules in a glove box and loaded into tubes to form beds for desorption, figure 2. Using mass flow controllers, a metered flow of carrier gas is feed through the adsorption bed at a constant temperature, maintained by the environmental chamber. A nitrogen by-pass is used to maintain atmospheric pressure in the system, while insuring that no contaminants are introduced through the open tee by providing an excess of carrier gas to be vented to the atmosphere. The vapor phase is concentrated and analyzed by purge and trap chromatography using a thermal desorption apparatus (Dynatherm) and the GC.

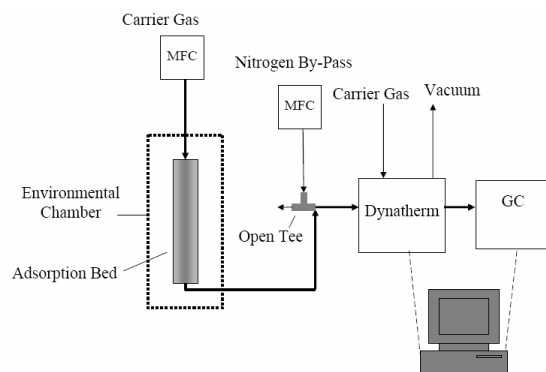


Figure 2. Schematic diagram of desorption apparatus.

3. RESULTS

This work has focused on the measurement of data for three compound classes in an effort to determine transitions from a Potential Theory-type pore filling correlation to HL behavior. To that end, research procedures have been developed for the preparation of adsorbent samples that can be used for accurate ultra-low concentration adsorption equilibrium measurements. We have also developed a framework for interpreting the data.

It is difficult to predict where theories will start to deviate from the experiments before data are measured, but Henry's law can still be examined in the context of the theories. They vary in the region where the transition to Henry's law occurs. For the various theories, the Henry's law region was identified on a plot where n/P vs. n has a slope closely approaching zero. For our experiments, the Henry's law transition should occur first (i.e., at the highest loading) for *n*-pentane at 100C. For GCT, the transition occurs at 10^{-3} mol/kg for *n*-pentane. For the DR equation, the transition toward more linear behavior occurs around 5×10^{-5} mol/kg (and then continues to exhibit meaningless behavior as the isotherm slope approaches zero). The transition may change for GCT and VGT once the parameters can be refit to account for the low concentration data.

Table 1. Summary of Adsorption Conditions

Adsorbate	Adsorbent	Loading Range (wt %)	Temperatures (C)
GB	Amborsorb 572	2, 2.5, 4.5	35-50
HD	Amborsorb 563	10, 14, 17	35-50
<i>n</i> -pentane	BPL	0.001-10	0-175
<i>n</i> -hexane	BPL	0.01-10	0-100
<i>n</i> -octane	BPL	0.01-10	0-100
<i>n</i> -decane	BPL	0.01-10	0-100

Uniformly loaded and measured AE data adsorbate-adsorbent pairs are shown in Table 1. The adsorption equilibrium data of GB measured on Amborsorb 572 has been examined for thermodynamic behavior. In the low concentration limit adsorption on a homogeneous or heterogeneous surface should approach a Henry's law limit. While inorganic adsorbents such as BPL activated carbon contain large fractions of inorganic impurities, polymeric adsorbents such as Amborsorb offer a cleaner surface. The data measured for GB is shown in figure 3 at three temperatures as partial pressure versus loading and is plotted together with earlier data measured gravimetrically. The units of Pa and mol/kg are the appropriate SI representation of adsorption equilibria. However most theories suggest that adsorption behavior is dependent on relative pressure. The relative pressure for GB at the Short Term Exposure Level, STEL concentration of 1×10^{-4} mg/m³, is 4×10^{-9} or partial pressure 1.6×10^{-6} Pa which corresponds to a partial pressure of 9.6×10^{-5} and 3.11×10^{-4} Pa for hexane and pentane at 25 C. In the Henry's law limit the slope of this line should approach 1, indicating a linear dependence of vapor concentration on loading. Though data are limited to three loadings at each temperature the trend clearly shows that over the range considered, the data are not low enough to exhibit a slope of 1 for Henry's law behavior.

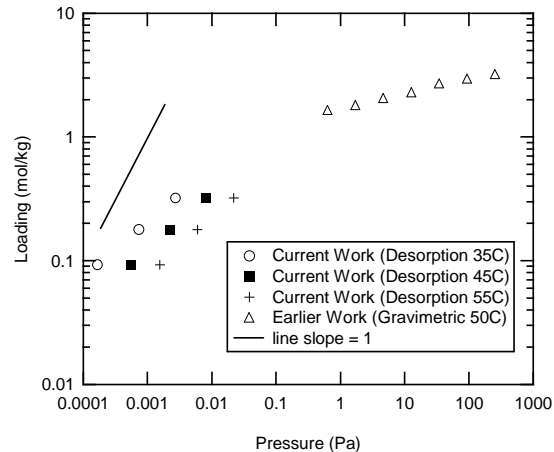


Figure 3. Adsorption Equilibrium of GB on Amborsorb 572.

The two lightest *n*-alkanes considered are *n*-pentane and *n*-hexane. Earlier hexane adsorption equilibrium data were measured using volumetric systems by Rudisill et al., 1992, and Karwacki (unpublished data). Figure 4 shows adsorption equilibrium data and the currently best available predictions for *n*-hexane adsorbed on BPL activated carbon at 25C. Predictions of these data are also shown using the DR equation and our methods of the GCT, and VGT. The figure also shows a line of slope unity, i.e., linear on rectangular coordinate system, which

must be approached at very low concentrations based on theoretical considerations. Both the GCT and the VGT approach this limit. Figure 5 shows the adsorption equilibrium data for n-pentane on BPL activated carbon at 25 C. Also shown is the DR predictions and a line of slope unity. Figures 6-7 show the approach to the Henry's Law region for n-hexane and n-pentane, respectively. When the data is plotted as n/P vs. n , Henry's Law is approached as the slope of the curve goes to zero. It can be seen that Henry's law region has not been achieved. Also, the Henry's Law region will be achieved sooner for n-pentane than for n-hexane, and it will be achieved sooner at higher temperatures.

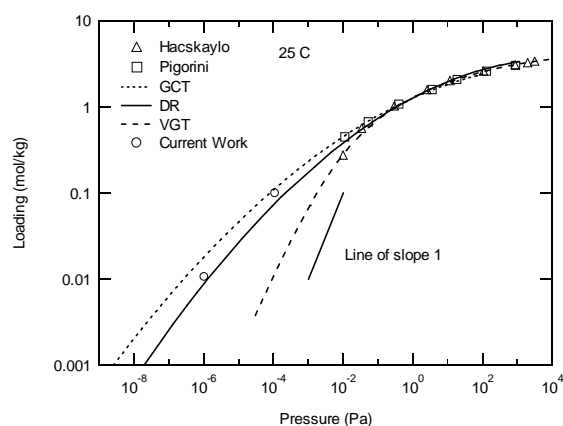


Figure 4. Adsorption equilibrium of n-hexane on BPL carbon at 25C.

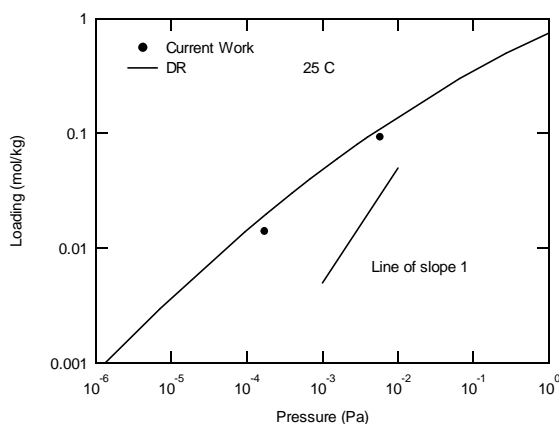


Figure 5. Adsorption equilibrium of n-pentane on BPL carbon at 25C.

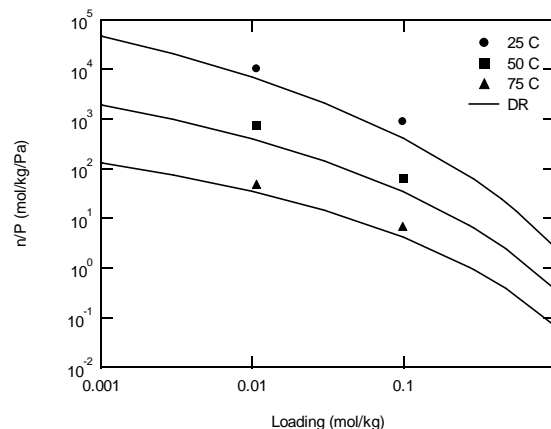


Figure 6. Approach to Henry's Law region for n-hexane.

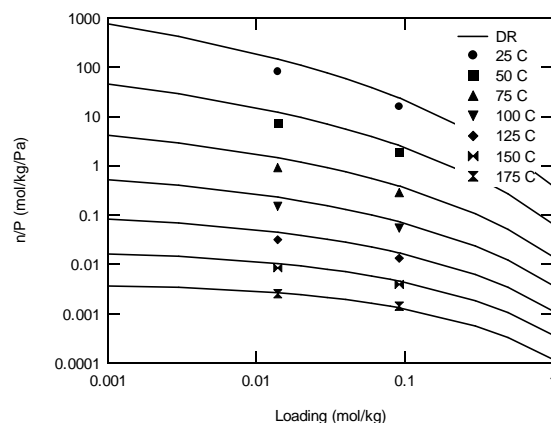


Figure 7. Approach to Henry's Law region for n-pentane.

4. CONCLUSIONS

Here new data at ultra-low concentrations has been measured and validated. Comparison with existing prediction methods and improved methods for predicting adsorption equilibrium at ultra-low concentrations. This effort will focused on a comparison study of the two adsorbent loading techniques: ampule and fluidization. It also discussed equilibria for a more volatile alkane and lower loading of chemical agents. Performance of the work requires state-of-the-art analytical systems developed at ECBC for the detection of nerve agents at extremely low concentration levels.

All of the models describe the historic data well at high concentrations. What is apparent, however, is that the predictions diverge widely at low concentrations. Also shown on figure 4 is our currently lowest measured point, shown as a circle, for which the loading is 0.10 mol/kg (0.86 weight %). The y-axis in Figure 4 includes the complete lower range over which samples have been prepared (i.e., down to 0.001 mol/kg) and which will be experimentally accessible using our methods. It should be noted that the predictions vary by nearly three orders

of magnitude at this lowest loading (corresponding to 1 ppT) which is well within the range of current concern for air monitoring applications noted above. Follow-up research would focus on the investigation of other organic compounds, or multicomponent investigations of hydrocarbons, or with water.

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